Processing, Mechanical Properties, and Fracture Behavior of Cereal Protein/Poly(hydroxyl ester ether) Blends*

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ABSTRACT: Blends of poly(hydroxy ester ether) (PHEE), a recently developed bisphenol A ether-based synthetic biodegradable thermoplastic polymer, with a soybean protein isolate and two hydrolyzed wheat glutens were studied. Blends of the proteins with PHEE were produced from 20 to 70% by weight of protein content. Young's moduli of the protein/PHEE blends fall in the range of 0.8–1.5 GPa with tensile strengths ranging from 10 to 30 MPa. Critical stress-intensity factors of the blends ranged from 2 to 9 MPa-$m^{1/2}$ depending on the amount of protein added. Morphological analysis indicated a moderate degree of adhesion between the protein and PHEE phases in the blends. In general, as the protein content was increased the materials lost ductility and failed in a brittle manner; however, the mechanical properties of several compositions were comparable to commercial thermoplastics such as polystyrene. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 2324–2332, 2002

Keywords: blends; proteins; fracture; soybean; wheat; mechanical properties

INTRODUCTION

The United States is both the biggest consumer of petroleum and the overseer of the largest farm product surplus in the world. In recent decades, the prices of farm products have tended to decrease as dramatic increases in the price of petroleum have taken place. The environmental impact of petroleum-based disposable items is also becoming a worldwide problem.[1] Utilization of farm products to lessen the dependence of petroleum resources is of great interest to both environmentalists and farmers in the United States. If plant-based biodegradable materials can be developed that are competitive in terms of both cost and performance, new markets for these renewable resources will be opened.

Renewable resources from farm products, such as starches and proteins, are more naturally abundant and economically feasible to use than many other biopolymers such as poly(lactide) or poly(hydroxybutrate).[2,3] Various starches and proteins are now being used as alternatives in the manufacture of adhesives, coatings, plastics, and binders. Although pure proteins are relatively more expensive than petroleum resources, some protein-containing materials are relatively inexpensive. Soybeans contain about 40% by weight of various proteins. Its price ($0.80/lb) is comparable to conventional petroleum-based resins ($0.50/lb).[4]

*Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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The United States produced nearly 50% of the soybeans grown in the world last year, and new industrial uses need to be discovered for this important crop.[5]

Utilization of cereal proteins in nonfood industrial applications has been an area of recent research efforts. The use of protein-based materials in industrial applications faces many problems. Unlike traditional thermoplastics, cereal proteins do not flow readily without the addition of plasticizers making injection and compression molding difficult if not impossible. The mechanical properties of cereal proteins are not as robust as those of traditional thermoplastics. Cereal proteins are typically very brittle. Their mechanical properties degrade with storage and are affected by both temperature and humidity. The addition of plasticizers and/or crosslinking agents can be used to address some of these problems.

In 1994, Paetau et al.[6] investigated biodegradable plastic products produced from soybean proteins. They explored the processing conditions for making biodegradable materials from soybean protein isolates and soybean protein concentrates at different moisture and acid levels. They also evaluated the impact of the processing conditions on their physical properties. The researchers measured the tensile modulus, yield strength, percent elongation, and water absorption of the molded samples. They found that the acidic level had a crucial impact on the mechanical properties and water absorption. Optimum mechanical properties were obtained at pH = 4.5 around the isoelectric point of soybean protein.

In 1997, Bassi et al.[7] disclosed an approach to produce grain protein-based articles. In this patent, grain proteins were blended with starch, water, and plasticizer to form solid, nonedible biodegradable, grain protein-based articles. The investigators used water and other polar solvents in amounts from 10 to 40% by weight as plasticizers to produce materials that could be compression- and injection-molded.

One method to introduce cereal proteins into the engineering thermoplastics market is to use them in blends and composites. In 1998, John et al.[8] reported their work on the processing of blends of wheat gluten and modified polycaprolactone (PCL). The researchers injection-molded the blends into testing samples and examined the tensile and flexural properties. They discovered that a small amount of anhydride-modified PCL in the blends resulted in improvement in the tensile modulus of nearly one order of magnitude. In the same year, a group of researchers[9] at Kansas State University investigated glass-filled soybean protein composites. The composites were produced with an autoclave, and glycerol was used as a plasticizer. They also used aminopropyl-trimethoxy silane to improve the adhesion between the soybean protein matrix and the glass fiber. The resulting materials had initial toughness values comparable to commercial glass-filled epoxies and thermoplastics.

The utilization of proteins directly as engineering materials faces several challenges including poor mechanical properties; however, it has been shown that proteins can be molded into blends with other materials and yield resins that possess performance characteristics comparable to those of commercial engineering thermoplastics. One of the issues with many protein-based blends is obtaining acceptable adhesion with the other components of the blend. In addition, issues of thermal and environmental stability of the materials also may limit the field of application.

In this article, initial studies of the processing and physical properties of cereal protein/poly(hydroxyl ester ether) (PHEE) blends are reported. PHEE is a bisphenol A ether-based synthetic biodegradable thermoplastic polymer that has been developed by Dow Chemical Company.[10] PHEE has a number of interesting physical properties, not the least of which is its biodegradability, that make it a desirable choice for use in blends with various agricultural polymers. Recent studies of this material blended with starch have shown that composites may be made with acceptable levels of adhesion between the two phases and with mechanical and rheological behavior comparable to commercial engineering thermoplastics.[11,12] This article presents the first efforts to produce protein-based PHEE blends with similar competitive properties.

MATERIALS AND METHODS

Samples

Soybean protein isolates (EDI Pro A) and two hydrolyzed wheat glutens (Flavor Pro 400 and Flavor Pro 1000) obtained from Protein Technologies International (St. Louis, MO) and Midwest Grain Products, Inc. (Atchison, KS), respectively, were used. All of the materials contained 6.0 $\pm$ 1.0% moisture by weight, using the procedure described subsequently, and were used as re-

Table 1. Physical and Chemical Properties of Commercial Proteins

Symbol	EDI Pro A	FP400	FP1000
Modified by vendor	No	Yes	Yes
Degree of hydrolization (%)	Not applicable	10–12	~5
MC (%)	6.0 ± 1.0	6.0 ± 1.0	6.0 ± 1.0
Maximum weight percentage in PHEE (%)	70	70	70
Isoelectric Points	5.34 ± 0.11	6.71 ± 0.22	6.15 ± 0.10
(pH)	9.08 ± 0.11	8.56 ± 0.31	8.56 ± 0.40
T_D (°C)	>175	>180	>180
T_g (°C) at 50/50 wt % with PHEE	36.9 ± 0.7	33.6 ± 0.4	31.5 ± 0.6
T_p (°C)	120–170	120–140	130–150
Solubility (pH = 7.0)	Relatively low	Relatively high	Relatively high

T_D: Denaturation temperature from DSC. T_g: Glass-transition temperature from DSC. T_p: Processing temperature range.

ceived. PHEE was acquired from the Dow Chemical Company (Midland, MI). The physical and chemical properties of the various proteins are summarized in Table 1, and the chemical structure of PHEE is illustrated in Figure 1.

Moisture Analysis

The moisture content of the protein samples and the processed blends were analyzed with a Mettler–Toledo LJ-16 Moisture Analyzer (Greifensee, Switzerland). The analyses were conducted by measuring the difference in weight in the sample after exposure to 120 °C for 20 min. This procedure produced a stable, constant final weight for the sample indicating all of the moisture in the material had been purged. For each sample, three replicates were performed.

Extrusion

A ZSK-30 twin-screw extruder by Werner & Pfleiderer (Ramsy, NJ) was used to blend the proteins with PHEE. Temperatures at every region were set in the range of 120–140 °C. The screw was operated at a range of 100–150 rpm. The samples were fed at a rate of approximately 60 g/min. Blends with protein contents exceeding 70% by weight were difficult to process and required high torques to extrude the materials. Therefore, the protein content examined in this study was limited to a maximum of 70% by weight. The blends were chopped into pellets with a length less than 5 mm immediately after the extrusion. The pellets were stored in a vacuum dessicator under 1/10 of atmosphere pressure to remove the remaining moisture until further use. The moisture content of the extruded pellets averaged 3.8 ± 0.4% by weight and was reduced to 2.5 ± 0.2% by weight after storage in the dessicator.

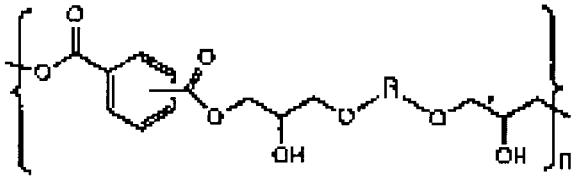


Figure 1. Chemical structure of PHEE.

Molding

Following the ASTM D638 method,[13] a Cincinnati Milacron Marketing Co. ATC-4.0-1.5 injection-molding machine (Batavia, OH) was used to produce ASTM Type C tensile bars at a fill pressure of 55 MPa. The molding temperature was carefully set in the range of 140–160 °C. The tensile bars were then stored at 25 °C and 50% relative humidity for 7 days before testing. The moisture content of the materials after conditioning and prior to mechanical testing was 4.4 ± 0.6% by weight.

Thermal Analysis

Thermal behavior of the proteins was analyzed with a TAC/DX PerkinElmer differential scanning calorimeter (DSC) (Norwalk, CT). Scans were conducted on each material at a rate of 10 °C/min. In addition, isothermal experiments were also performed where the heat flow was monitored over time at a constant temperature. For the isothermal experiments, data were taken 20

min after the scanning was initiated. Dry air was purged into a sample chamber at the rate of 5 cm^3/s. An opened cell was prepared by punching a hole with a 1-mm-diameter on the lid of the aluminum cell and used to compare the data obtained using sealed cells.

Fracture Measurements

An Instron 4201 (Instron Corp.) operating under Instron Series IX software control (Canton, MA) was used to evaluate the mechanical properties of various cereal protein/PHEE blends. In the fracture experiments, single-edge notch (SEN) samples were produced from the aforementioned tensile bars, which were 65.0 ± 5.0 mm in length, 12.7 ± 0.2 mm in width, and 2.74 ± 0.10 mm in thickness. A 2.0 ± 0.3 mm notch was made with a CS-93M-047 sample notching device by Customer Scientific Instruments, Inc. (Long Island, NY). A precrack with 0.2 mm in depth was made with a razor along the 2.74-mm side prior to the fracture testing. The measurements of critical stress-intensity factors, K_{1c}, and the energy-release rate to break, J^*, were carried out at a crosshead rate of 50 mm/min, 25 °C, and 50% relative humidity. Values for K_{1c} and J^* were obtained using

$$K_{1c} = C\sigma_c(\pi b)^{1/2} \quad (1)$$

and

$$J^* = \frac{U}{(a - b)(c)} \quad (2)$$

where a is the width of the sample, b is the depth of the notch, c is the thickness of the sample, U is the energy obtained from the area of the stress-strain curve, σ_c is the stress at failure, and C is a constant related to the geometry of the sample.[14] The broken tensile bars were retained for morphological analyses.

Morphological Analysis

Fracture morphologies of blends were investigated with a JSM-6400 JEOL scanning electron microscope by JEOL Ltd. (Zephyr, TX). The fracture surfaces of the samples were sputter-coated with a 20-nm-thick gold–palladium coating. A DSC-460 digital camera by Eastman Kodak (Rochester, NY) was used to record the images of the fracture surfaces. Photographs of the fracture surface were taken at various magnifications along the fracture plane of each sample.

Rheological Measurements

An ARES Series IV mechanical spectrometer by Rheometric Scientific (Piscataway, NJ) equipped with a torsion rectangular fixture was used to determine glass-transition temperatures (T_g's) from the point where the ratio of the loss modulus to the elastic modulus was a maximum. The experiments were conducted at 0.05% strain, an oscillatory frequency of 1 rad/s, and 1 °C/min from 0 to 80 °C.

Solubility

Solubility of the proteins in aqueous solutions was determined with a UV160 by Shimadzu Scientific Instruments, Inc. (Wood Dale, IL). The protein was dissolved in deionized water at different pH values and then centrifuged at 80,000 rpm for 25 min in a TL-100 ultracentrifuge by Beckman Instruments (Palo Alto, CA). Hydrogen chloride and sodium hydroxide from Fisher Scientific (Fair Lawn, NJ) were used to adjust the solution to the desired pH range. A Fisher Scientific pH meter (model 25) was used to measure the pH value. The relative solubility of various proteins was determined from their relative absorption values at 280 nm. The solubilities of the three proteins at a pH of 7.0 are given in Table 1.

RESULTS AND DISCUSSION

DSC data were used to establish the optimal processing and molding temperatures for each of the cereal proteins (Table 1). No significant differences were found between using sealed and open DSC cells. In both extrusion and molding, the EDI Pro A/PHEE blend was difficult to mold below 120 °C and experienced noticeable denaturation at temperatures over 175 °C. The feasible processing temperature for the EDI Pro A/PHEE blend falls in the range of 140–165 °C. In this range, the system does not suggest any significant denaturation for hours. The blends produced using FP400 and FP1000 also displayed similar temperature stability, and these blends were also produced using the temperature range noted previously.

The effect of temperature on the oscillatory storage and loss moduli as well as the tangent

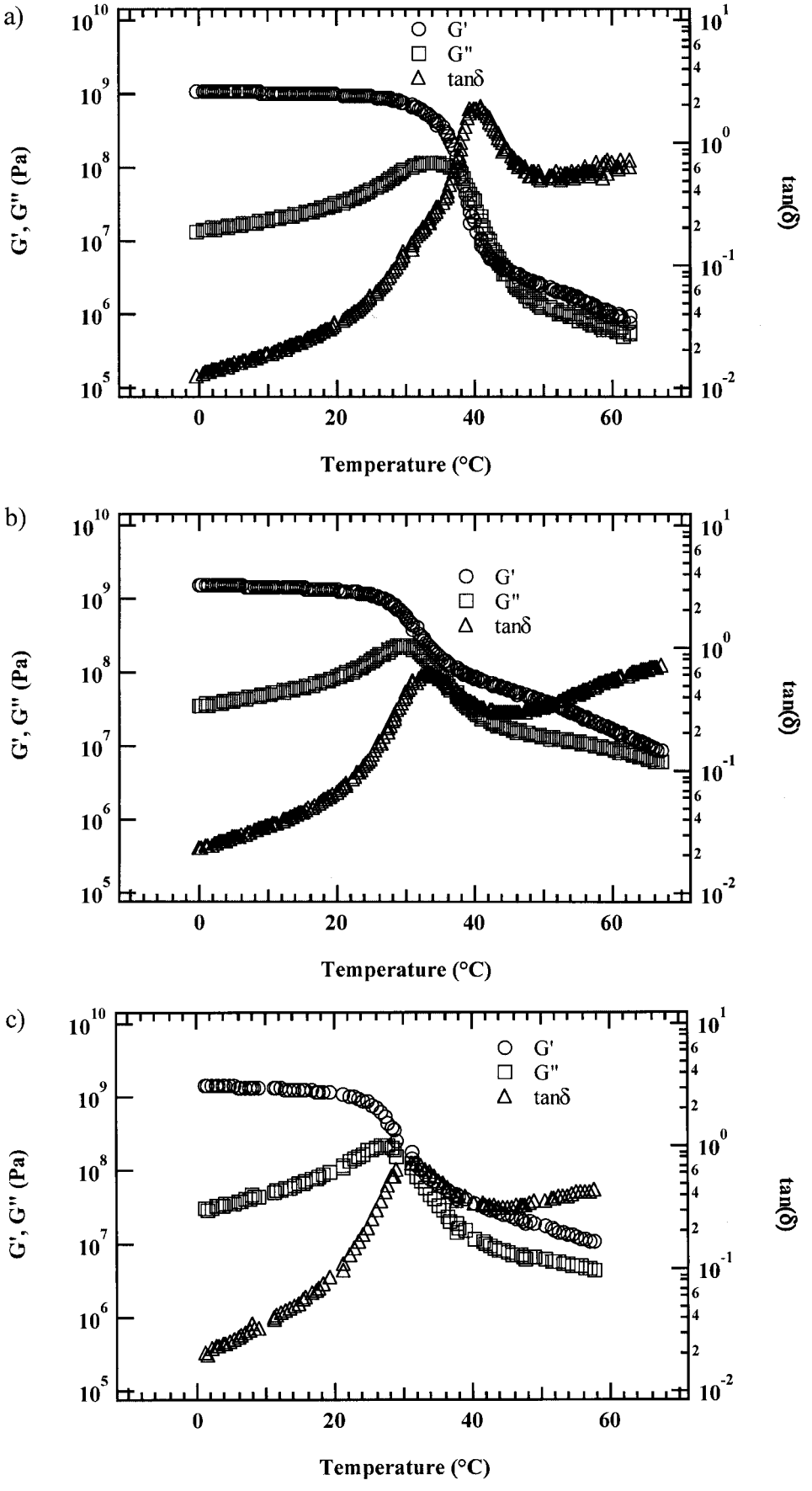


Figure 2. Effect of temperature on the viscoelastic properties of a) 50/50 EDI ProA/PHEE, b) 50/50 FP400/PHEE, and c) 50/50 FP1000/PHEE blends.

phase angle is displayed in Figure 2 for 50/50 blends of EDI ProA/PHEE, FP400/PHEE, and FP1000/PHEE. At temperatures from 0 to 37 °C, the blends display a glassy storage modulus with a magnitude of about 1 GPa, which is in accord with commercial thermoplastic-based blends. As the temperature is increased, the glassy storage modulus remains independent of temperature up to approximately 37–39 °C (the T_g of PHEE) at which point the modulus is observed to drop rapidly to approximately 3 MPa at 42 °C. As the temperature is increased above 42 °C, the modulus continues to decrease gradually with increasing temperature. The T_g of the blend is observed at 37–40 °C depending of whether one takes the transition at the peak of G'' or at the peak of tan δ. The T_g's of the three blends at 50/50 weight ratios are summarized in Table 1.

The effect of blend composition of Young's modulus for the three protein/PHEE blends is illustrated in Figure 3. Within the experimental error, all of the blends displayed similar moduli values. The blends all displayed a slight increase in the modulus with an increasing protein content with the moduli ranging from 0.9 ± 0.04 GPa for pure PHEE up to 1.5 ± 0.05 GPa for 70% by weight FP400/PHEE. In contrast, the addition of the various proteins to PHEE caused a sharp drop in the measured tensile strength of the blends from 47

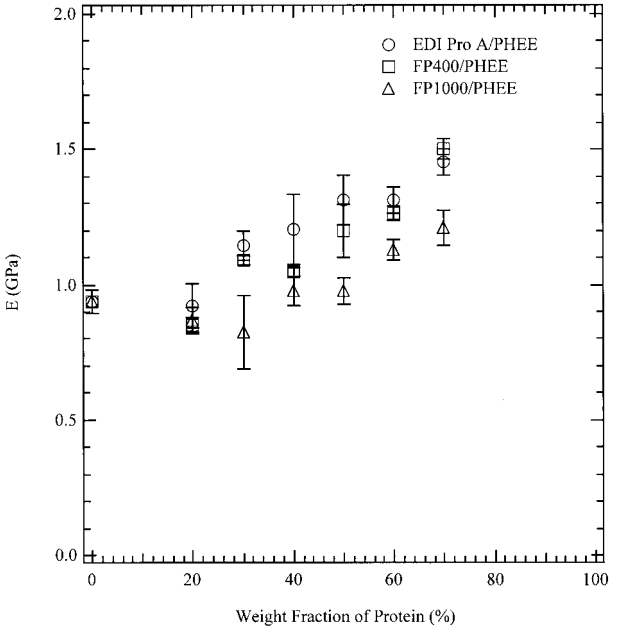


Figure 3. Effect of composition on Young's modulus for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends.

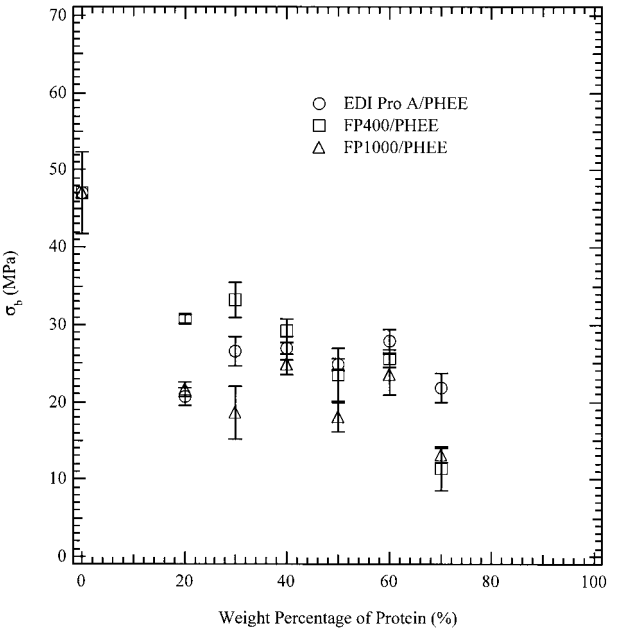


Figure 4. Effect of composition on the tensile break strength for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends.

± 5 MPa for pure PHEE to 22 ± 2 MPa for a EDI Pro A/PHEE blend containing 70% by weight protein (Fig. 4). At a composition of 70% by weight, the FP400/PHEE and FP1000/PHEE blends displayed tensile break strengths of 11 ± 3 and 13 ± 1 MPa, respectively. The drop in the tensile break strength was accompanied by a slight increase in the tensile elongation of each of the blends (Fig. 5). The tensile elongation of the pure PHEE resin was 1.0 ± 0.1%. As the protein content in the blends was increased to 70% by weight, the tensile elongation of the blends reached 1.45 ± 0.06, 1.50 ± 0.04, and 1.20 ± 0.065% for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE, respectively. In addition, none of the blends displayed any evidence of yielding; all of the blends failed in a brittle manner.

The effect of composition on the critical stress-intensity factor, K_{1c}, is illustrated in Figure 6. An evaluation of the K_{1c} value for pure PHEE was not possible because of the presence of slight yielding in the samples. As the protein content is increased, the measured K_{1c} values for the blends dropped slightly. The blends produced with EDI Pro A displayed the least amount of change. At a composition of 30:70 by weight EDI Pro A/PHEE, the K_{1c} value was 3.9 ± 0.4 MPa-$m^{1/2}$. When the concentration of EDI Pro A was raised to 70% by

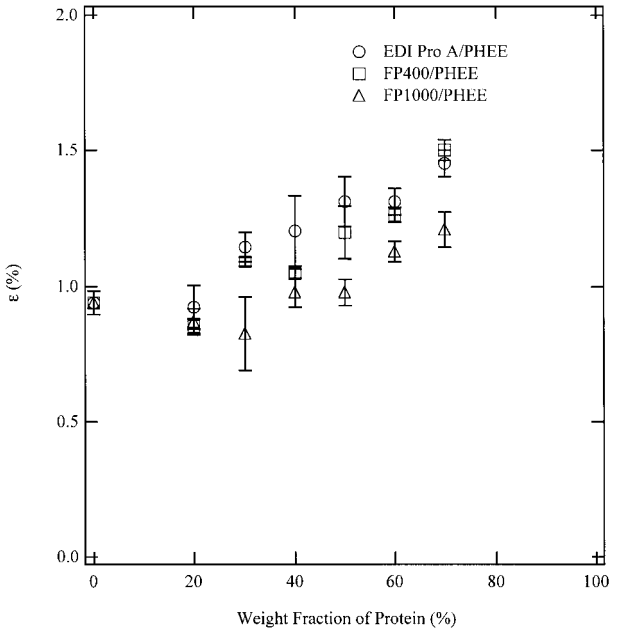


Figure 5. Effect of composition on the tensile elongation for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends.

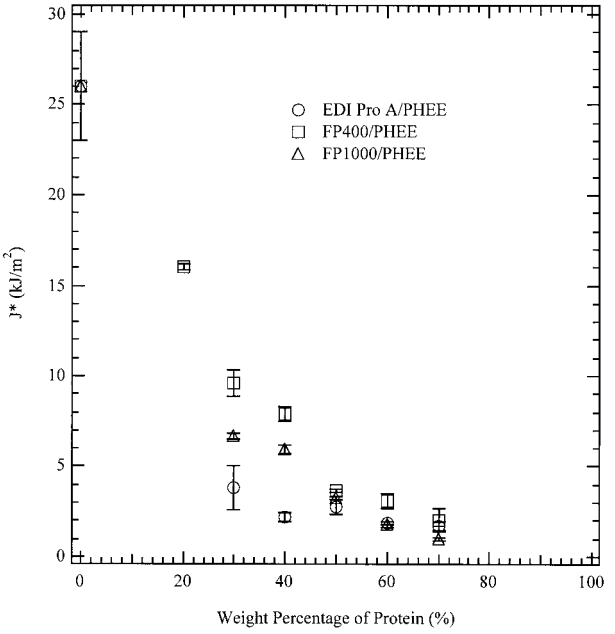


Figure 7. Effect of composition on the energy-release rate to break for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends.

weight, the K_{1c} value was 4.4 ± 0.8 MPa-m$^{1/2}$. For the FP400/PHEE blends, the K_{1c} value at a protein content of 20% by weight was 9.4 ± 1.0 MPa-m$^{1/2}$, which is markedly higher than the K_{1c} value for EDI Pro A/PHEE at the same level of protein addition. When the protein composition was raised to 70% by weight, the value for K_{1c} dropped to 3.0 ± 0.6 MPa-m$^{1/2}$, roughly comparable to the value obtained with EDI Pro A at the same composition. For the FP1000/PHEE blends, the value of K_{1c} went from 5.6 ± 0.2 MPa-m$^{1/2}$ at 20% by weight of protein to 2.3 ± 0.2 MPa-m$^{1/2}$ at a protein composition of 70%. In comparison, commercial thermoplastics such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) have quoted K_{1c} values, evaluated using SEN geometry, of 0.6–2.3 and 1–3.5 MPa-m$^{1/2}$, respectively.[15] Clearly, the fracture strengths of the protein/PHEE blends are comparable to PS and PMMA.

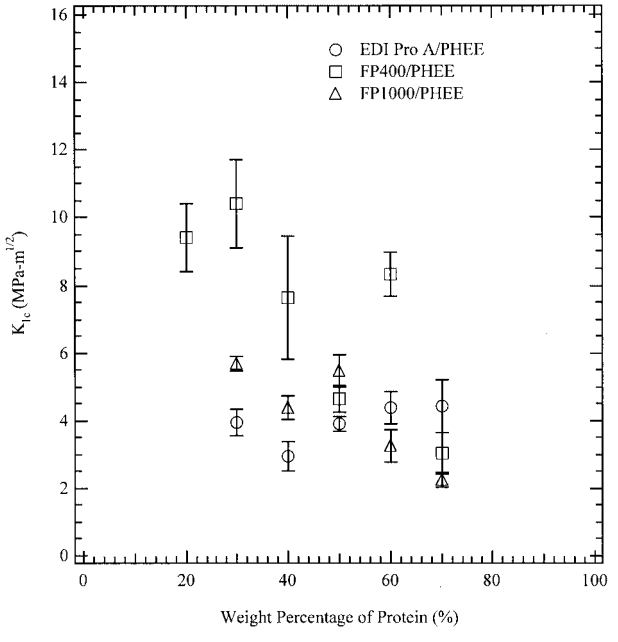
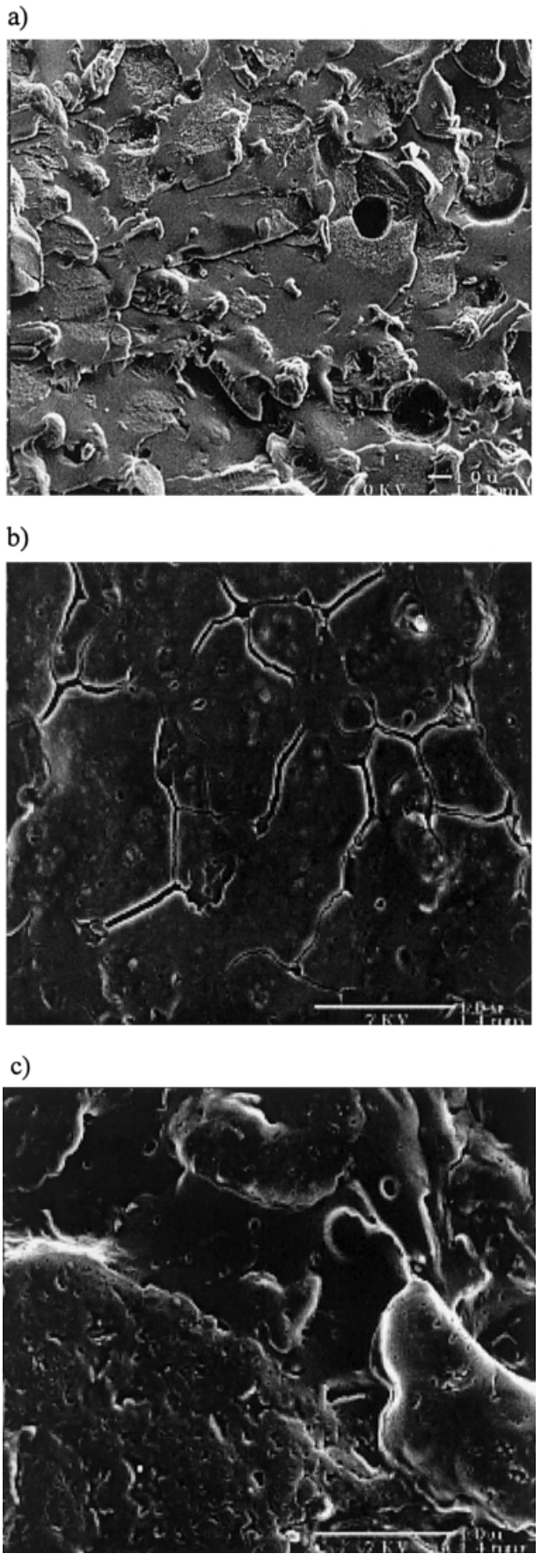


Figure 6. Effect of composition on the stress-intensity factor for EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends.

The effect of composition on the energy-release rate to break, J^*, is illustrated in Figure 7. Pure PHEE was observed to yield a J^* value of 26 ± 3 kJ/m^2. The values of J^* decrease rapidly with an increasing weight fraction of protein for both the FP400/PHEE and FP1000/PHEE blends. At a composition of 20% by weight of protein, J^* values were 9.6 ± 0.7 and 6.7 ± 0.1 kJ/m^2, respectively. As the protein content was increased to 70% by weight, the value of J^* fell to 2.0 ± 0.6 and 1.0 ± 0.1 kJ/m^2. For the EDI Pro A/PHEE blends, J^* displayed less dependence on the protein content than did the blends produced with hydrolyzed wheat proteins. J^* values for the EDI Pro



A/PHEE blends ranged from 3.7 ± 0.12 at 30% by weight of protein to 1.7 ± 0.2 kJ/m^2 at 70%.

The fracture surfaces of the cereal protein/PHEE blends were examined microscopically with scanning electron microscopy (SEM). The fracture surfaces of EDI Pro A/PHEE, FP400/PHEE, and FP1000/PHEE blends, each containing 50% by weight protein content, are illustrated in Figure 8. In the micrograph for the 50/50 EDI Pro A/PHEE blend (500×), several large holes are evident where the protein aggregate has been pulled out from the blend matrix. Around these holes there appears to be little evidence of localized yielding. This observation is consistent with the low values for the measured fracture strength of the material indicating pure brittle failure. Also evident in the figure are several areas that appear to be the remnants of fractured protein aggregates. These fractured aggregates indicate that some degree of moderate adhesion between the EDI ProA protein and PHEE phases was obtained. In the micrographs for the 50/50 FP400/PHEE and FP1000/PHEE blends, the areas for dislocation of the protein aggregates that were observed in the EDI ProA/PHEE blend were not observed. The fracture surfaces for both the blends do not show any evidence for localized yielding, which is consistent with the low fracture strengths measured for these materials.

CONCLUSIONS

This work has shown that selected cereal proteins can be used in combination with PHEE to produce thermoplastics blends. The blends possess acceptable mechanical properties yielding values for the tensile moduli, tensile break strengths, and fracture strengths that are comparable to commercial thermoplastic materials. The blends were produced with commercial extrusion and molding equipment and did not require the addition of plasticizers. Micrographs of fracture surfaces indicated that some degree of moderate adhesion between the PHEE and the three proteins was obtained.

Although the blends possessed toughness values comparable to thermoplastics such as PS, ef-

Figure 8. Fracture surface (500×) of a) 50/50 EDI Pro A/PHEE, b) 50/50 FP400/PHEE, and c) 50/50 FP1000/PHEE blends.

fective toughening strategies will have to be developed to make these materials competitive in traditional engineering markets. In addition, studies on the effects of physical aging and long-term retention of mechanical properties will need to be conducted. Immediate future work will focus on a more detailed understanding of the failure mechanisms for these blends and the development of optimized toughening strategies.

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